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^{57}Fe MÖSSBAUER SPECTROSCOPY OF MONTMORILLONITES: A NEW INTERPRETATION

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Abstract—The ^{57}Fe Mössbauer spectra of several montmorillonites, measured at room temperature and 453 K, showed a considerably broadened Fe^{3+} resonance which can be computer-fitted with a similarly broadened Fe^{3+} doublet. In some spectra, particularly if all linewidths were constrained to be equal, this broadened Fe^{3+} resonance was further resolved into overlapping inner and outer Fe^{3+} doublets, also having broad linewidths. In accordance with recent electron diffraction evidence, the assignment by previous workers of the inner doublet to Fe^{3+} in the octahedral sites having the cis-arrangement of OH groups and the outer doublet to the octahedral site having the trans-arrangement of OH groups is incorrect. Instead, the Fe^{3+} was found to be located largely in the trans-octahedral sites. Because of the relatively low iron content of the montmorillonite examined, the next and more distant neighboring-cation environment varied considerably about the octahedral Fe^{3+} ions. This variation produced a broadened experimental resonance, and the resulting two-doublet computer fits probably represent the mean extremes of a continuum of slightly different Fe^{3+} resonances arising from the variable nature of the environment surrounding these such trans-sites, rather than distinct cis- and trans-sites. In addition, a small resonance indicating the substitution of Fe^{3+} into the tetrahedral sites was observed. The interlayer species probably influenced the Mössbauer resonance of Fe^{3+} in the tetrahedral and octahedral sites.

Key Words—Iron, Montmorillonite, Mössbauer spectroscopy, Octahedral sites, Tetrahedral sites.

INTRODUCTION

Montmorillonite is a common member of the smectite group of phyllosilicates. It has an idealized dioctahedral end-member composition of $Al_4Si_8O_{20}(OH)_4 \cdot n\,H_2O$; however, some Mg^{2+} generally substitutes for Al^{3+} in the octahedral layer, the charge deficiency being compensated by other cations, e.g., Ca^{2+}, Na^+, occupying interlayer positions. Such octahedral substitution may impart some trioctahedral character to the clay. Iron is also generally present, mostly as Fe^{3+}, which is invariably considered to occupy octahedral sites (e.g., see Brindley and Brown, 1980). Some Fe^{2+} has been identified in the interlayer (Helsen and Goodman, 1983). Minor amounts of Al^{3+} may substitute for Si^{4+} in the tetrahedral sites, but Fe^{3+} is usually considered not to occupy these sites. The montmorillonite composition is therefore expressed as

$$(\tfrac{1}{2}Ca,Na)_{0.7}(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4 \cdot n\,H_2O$$

In smectite the $AlO_4(OH)_2$ octahedra are arranged in sheets wherein ⅔ of the sites have a cis-arrangement of OH ions and ⅓ have a trans-arrangement. In essentially dioctahedral smectites, e.g., nontronite and montmorillonites, only about ⅔ of these sites are occupied by octahedral cations, and the question arises as to which of these sites are occupied.

The ^{57}Fe Mössbauer spectra of montmorillonites generally show a broadened Fe^{3+} resonance having, in some spectra, a minor Fe^{2+} component. Rozenson and Heller-Kallai (1977) computer-fitted such Fe^{3+} resonances to two overlapping Fe^{3+} doublets having about the same isomer shift (δ) values, but wherein the quadrupole interaction (Δ) values differed by about a factor of 2. The fitted doublet having the smaller Δ value comprised about ⅔ of the total experimental resonance area and was assigned to Fe^{3+} occupying cis-octahedral sites. Similarly, the doublet with the larger Δ value was assigned to Fe^{3+} in trans-octahedral sites. From these assignments they concluded that the Fe^{3+} is about evenly distributed throughout the two cis- and one trans-sites per formula unit. In their computer-fitting, however, Rozenson and Heller-Kallai (1977) constrained the linewidths of all the Fe^{3+} peaks to be equal. As discussed below, this constraint can have a profound effect on the results obtained.

Rozenson and Heller-Kallai (1977) obtained similar results for octahedral Fe^{3+} site occupancy of the iron-rich smectite, nontronite. Early electron diffraction work by Mering and Oberlin (1967), and more recently by Besson *et al.* (1983), showed the montmorillonite structure to be non-centrosymmetric; hence, both the cis- and trans-octahedral sites can be occupied by cations. The nontronite structure, however, has been found to be centrosymmetric, an arrangement that requires the trans-sites to be vacant (Mering and Oberlin, 1967; Besson *et al.*, 1983). This observation for nontronite was at variance with the conclusions drawn from the Mössbauer data. Goodman (1978) suggested the two computer-fitted Fe^{3+} doublets in the nontronite Möss-

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Table 1. Locations and compositions of montmorillonites.

Location	Wt. % Fe	Composition per $O_{10}(OH)_2$
Yavapai County, Arizona; Ward's Natural Science Establishment Rochester, New York	2.23	$(Na_{0.02}Ca_{0.10})(Si_{3.98}Al_{0.02})(Fe_{0.14}Al_{1.16}Mg_{0.90}Ti_{0.04})$
Wyoming; Ward's Natural Science Establishment Rochester, New York	3.52	$(Na_{0.07}K_{0.01}Ca_{0.17})(Si_{3.83}Al_{0.17})(Fe_{0.23}Al_{1.40}Mg_{0.42}Ti_{0.02})$
Husband Mine, Polkville Mississippi; No. 20. Ward's Natural Science Establishment Rochester, New York	5.44	$(Na_{0.02}Ca_{0.16})(Si_{3.87}Al_{0.13})(Fe_{0.35}Al_{1.36}Mg_{0.31}Ti_{0.02})$

bauer spectrum could have arisen from Fe^{3+} in the two cis-octahedral sites which were rendered inequivalent on a next-nearest neighbor basis as a result of the substitution of some Fe^{3+} in the tetrahedral Si^{4+} sites. Recent work by Johnston and Cardile (1985) and Cardile and Johnston (1985) on a suite of nontronites confirmed this interpretation and, in addition, showed that such inequivalence could also have resulted from, or have been enhanced by, the nature and position of the interlayer cation. As a result of detailed electron and X-ray powder diffraction studies and theoretical modeling, Tsipursky and Drits (1984) and Drits *et al.* (1984) showed that the trans-octahedral sites were vacant in all the nontronites and in some of the montmorillonites studied by them. In most of the montmorillonites, one of the two kinds of cis-sites was vacant; in some montmorillonites largely the trans-sites were occupied. The cation substitution in the octahedral sites in montmorillonite therefore appears to be more variable than for nontronite.

In this paper the results of a detailed ^{57}Fe Mössbauer spectroscopic study are presented, including a critical evaluation of the computer-based curve-fitting procedure for three montmorillonites from different locations and with different iron contents. The results are interpreted with reference to the above-mentioned recent diffraction studies.

EXPERIMENTAL

Montmorillonites from Yavapai County, Arizona; Wyoming; and Husband Mine, Polkville, Mississippi, containing from about 2 to 5% Fe were used in this study. Details of the locations and the structural formulae calculated in a conventional manner are presented in Table 1. The elemental compositions were determined by X-ray fluorescence analysis.

The ^{57}Fe Mössbauer spectra were recorded at room temperature (298 K) and at 453 K using an ELSCINT AME40C spectrometer and a $^{57}Co/Rh$ source. The spectra were recorded over a velocity range of ±2.7 mm/s to achieve a good definition of the broadened Fe^{3+} doublet and also over ±4.0 mm/s to check for the presence of Fe^{2+} resonances. All spectra showed the high-velocity component peak of the experimental Fe^{3+} doublet to be less intense than the low-velocity component (Figures 1–3). To ascertain whether or not this asymmetry was a result of preferred orientation arising from the platey nature of clay minerals, the plane of the holder containing the Wyoming sample was rotated 45° to the γ-ray beam and the spectrum recorded again (Figure 1b).

The velocity scale was calibrated with reference to elemental iron with the mid-point of the room-temperature, magnetic hyperfine iron spectrum defining zero velocity. The spectra were computer-fitted with a number of Lorentzian peak lineshapes using a non-linear χ^2 minimization procedure. To achieve convergence in all the fits it was necessary to constrain the widths and dips of the component peaks in a particular doublet to be equal. In some spectra, however, to ascertain the effects that the constraints had on the computer-fitting procedure and the resulting parameter values, the linewidths of all four Fe^{3+} peaks defining the two octahedral doublets were constrained to be equal. The 1% and 99% confidence limits for χ^2 are 574 and 427 for a 4-peak fit and 570 and 424 for a 6-peak fit, respectively. In order for the χ^2 value to measure the goodness of the fit, the validity of the computer-fitted model, and hence the degree of disorder within the structure, the spectra were all recorded to a suitably high background count of $4\text{–}5 \times 10^6$ counts per channel (Johnston and Cardile, 1985).

RESULTS AND DISCUSSION

The ^{57}Fe Mössbauer spectra for the Wyoming, Yavapai, and Husband Mine montmorillonites, recorded over the velocity range of ±2.7 mm/s are shown in Figures 1–3, respectively. All experimental spectra show a considerably broadened Fe^{3+} resonance with, as mentioned above, a definite asymmetry in the intensities of the component peaks. Because the spectrum of the Wyoming sample recorded with the plane of the sample at 45° to the γ-ray beam (Figure 1b) was identical to that recorded in the usual manner (Figure 1a), such asymmetry was not due to preferred orientation effects. The spectra recorded at ±4 mm/s velocity range showed

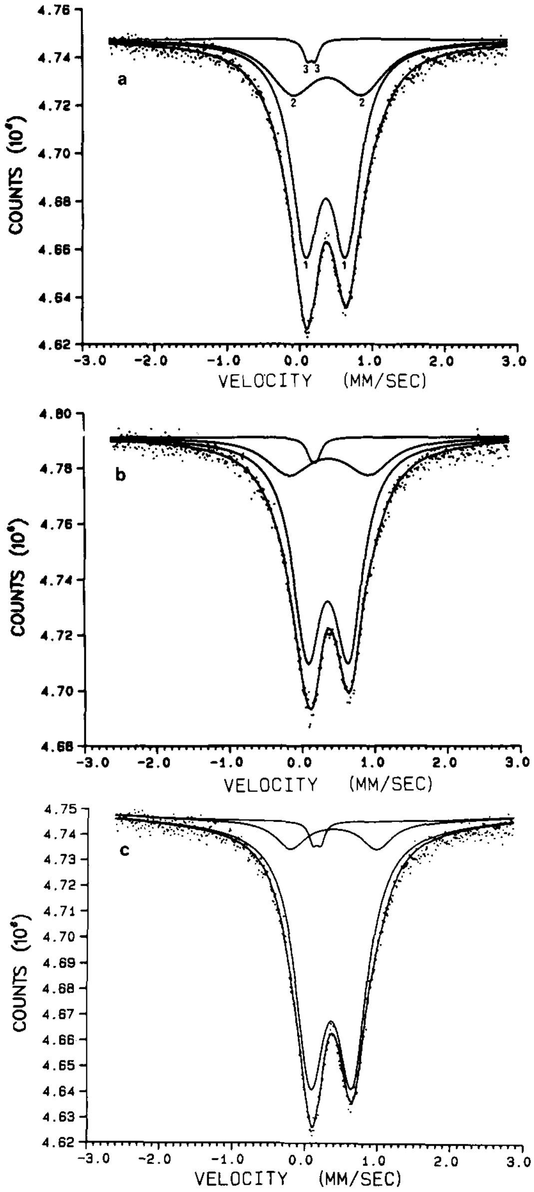

Figure 1. Experimental and computer-fitted ^{57}Fe Mössbauer spectra for montmorillonite from Wyoming: (a) sample plane normal to the γ-ray beam. 1 = inner-octahedral doublet, 2 = outer-octahedral doublet, 3 = tetrahedral doublet; (b) sample plane inclined 45° to the γ-ray beam; (c) widths of all the octahedral doublet peaks are constrained equal.

no high-velocity Fe^{2+} resonance, thereby confirming that this asymmetry was also not due to the presence of an overlapping low velocity component Fe^{2+} peak.

The spectrum for the Wyoming montmorillonite was computer-fitted with three overlapping Fe^{3+} doublets (Figure 1), initially with only the widths and dips of the component peaks in a particular doublet being constrained equal. The most prominent inner doublet 1 ($\delta = 0.35$, $\Delta = 0.56$ mm/s) and the outer doublet 2 (δ =

Table 2. Computer-fitted Mössbauer spectral data for montmorillonites.

		Inner-octahedral Fe^{3+} doublet				Outer-octahedral Fe^{3+} doublet				Tetrahedral Fe^{3+} doublet			
Sample[1]	χ^2	δ (mm/s)	Δ (mm/s)	Width (mm/s)	Rel. area	δ (mm/s)	Δ (mm/s)	Width (mm/s)	Rel. area	δ (mm/s)	Δ (mm/s)	Width (mm/s)	Rel. area
Wyoming[2]	539	0.35 (1)	0.56 (1)	0.48 (3)	69	0.37 (14)	0.96 (14)	0.77 (7)	29	0.15 (2)	0.11 (2)	0.13 (3)	2
Wyoming[3]	501	0.35 (1)	0.57 (1)	0.48 (2)	77	0.37 (13)	1.10 (13)	0.74 (12)	21	0.18 (3)	0.08 (3)	0.15 (6)	2
Wyoming[4]	547	0.35 (1)	0.58 (1)	0.50 (1)	88	0.38 (3)	1.19 (3)	0.50 (1)	10	0.15 (2)	0.11 (2)	0.13 (3)	2
Yavapai	534	0.33 (1)	0.53 (6)	0.61 (1)	98					0.14 (3)	0.12 (3)	0.15 (5)	2
Husband Mine	591	0.35 (1)	0.54 (1)	0.52 (1)	97					0.03 (1)	0.23 (1)	0.24 (2)	3
Husband Mine[4]	518	0.35 (1)	0.56 (1)	0.52 (1)	88	0.39 (4)	0.91 (4)	0.52 (1)	10	0.19 (1)	0.10 (1)	0.14 (2)	2
Husband Mine[5]	501	0.33 (3)	0.51 (3)	0.41 (5)	51	0.34 (8)	0.85 (8)	0.56 (5)	45	−0.06 (6)	0.52 (6)	0.29 (8)	3

[1] See Table 1 for locations.

[2] Sample plane normal to γ-ray beam.

[3] Sample plane inclined 45° to γ-ray beam.

[4] Widths of the inner- and outer-doublet peaks constrained equal.

[5] Spectrum recorded with sample at 453 K.

0.37, $\Delta = 0.96$ mm/s) were consistent with Fe^{3+} in octahedral O,OH coordination, and the smallest doublet 3 ($\delta = 0.15$, $\Delta = 0.11$ mm/s) was assigned to Fe^{3+} in tetrahedral coordination (Figure 1, Table 2). The linewidths (0.48 mm/s) of the peaks defining the inner doublet were broader than those observed for the inner doublet of nontronite (0.32 mm/s; Johnston and Cardile, 1985) and for primary silicate minerals (about 0.3 mm/s; see, e.g., Bancroft, 1973). The linewidths (0.77 mm/s) of the outer doublet were also much broader. This broadening is indicative of a considerable degree of structural disorder or differing environments around the respective Fe^{3+} ions in the structure. The inner doublet comprised 69% of the overall resonance area, the outer doublet 29%, and the tetrahedral doublet, 2%, respectively.

When the linewidth of the four peaks of these inner and outer doublets were constrained equal, consistent with the approach used by Rozenson and Heller-Kallai (1977), the respective Δ parameters assumed slightly larger values (Table 2). Also, the areas changed, and the inner doublet comprised 88% of the overall resonance area and the outer doublet only 10%. The tetrahedral resonance area of 2% remained unchanged (Table 2). The χ^2 value for the more fully constrained fit was higher than the value for the lesser constrained fit. These results suggest that (1) the most correct fit was that which required the least number of constraints to achieve convergence, and (2) the use of constraints can lead to different and probably less correct values of the fitted parameters. In the computer-fitting of Lorentzian peak lineshapes to such a broadened experimental resonance, the parameters for the less intense outer doublet assumed appropriate values, depending upon the constraints used, to account for the broadening at the base of this experimental resonance.

It is perhaps most convenient to assign the inner doublet to Fe^{3+} in the cis-octahedral sites and the outer doublet to Fe^{3+} in the trans-octahedral sites (Rozenson and Heller-Kallai, 1977). Johnston and Cardile (1985), however, showed that for nontronite two non-equivalent cis-octahedral sites exist. Numerous attempts to resolve this inner montmorillonite doublet further into two such cis-doublets giving three octahedral doublets overall were unsuccessful. If this two-octahedral-doublet model for Wyoming montmorillonite is correct, a comparison of the Δ values with those of nontronite suggests that only one of the two possible cis-octahedral sites as well as the trans-octahedral sites were occupied by Fe^{3+}. The unusually broad linewidths, however, indicate that the environment of these Fe^{3+} ions, probably on a next-nearest or more-distant neighbor basis, was extremely varied. This situation probably arose from the low population of Fe^{3+} ions in the structure. Because of the presence of other octahedral cations (Al^{3+}, Mg^{2+}), different neighboring tetrahedral cations (Al^{3+}, Fe^{3+}, Si^{4+}), and interlayer cations (Na^{+}, Ca^{2+}, etc.), a large variety in the next- and more-distant neighbor ions and in the arrangements of such ions about each octahedral Fe^{3+} was present. Hence, each Fe^{3+} experienced a slightly different electric field gradient which produced a correspondingly slightly different quadrupole splitting value. Such influencing effects from neighboring tetrahedral cations and more distant interlayer cations have been observed in nontronite (Johnston and Cardile, 1985; Cardile and Johnston, 1985). Because of this range of environments and resulting line broadening, the question arises as to whether or not it is correct to assign these two computer-fitted doublets to Fe^{3+} in specific cis-octahedral and trans-octahedral sites.

An alternative model is that a complete continuum of octahedral sites, either cis- and trans-, or trans- only, exist having slightly different types and arrangements of neighboring ions. This model gives rise to a considerably broadened Fe^{3+} resonance that can be satisfactorily computer-fitted with two overlapping Fe^{3+} doublet components, each with a reasonably wide linewidth. The outer doublet assumes the wider linewidth, however, to account for the broadening at the base of the experimental resonance. It is therefore more correct to computer-fit a distribution of doublets, having similar isomer shifts but slightly different quadrupole interactions, to this broadened experimental Fe^{3+} resonance, rather than two discrete doublets. Due to the limited computing resources available for this study, a computer-fitting of such a distribution of doublets was not possible. This model is analogous to that proposed for ferrihydrite in which the outer and inner doublets computer-fitted to a broadened experimental Fe^{3+} resonance were considered to represent the mean extremes of the lesser and more distorted sites of a continuum of sites arising from the poorly ordered nature of the material (Johnston and Lewis, 1983, 1986).

This latter interpretation is in contrast with that offered for nontronite (Johnston and Cardile, 1985) in which the experimental Fe^{3+} resonance was computer-fitted with two prominent overlapping Fe^{3+} octahedral doublets and a tetrahedral and interlayer doublet. The octahedral doublets had considerably narrower linewidths (inner doublet 0.32 mm/s; outer doublet 0.32 mm/s), comparable with those of Fe^{3+} in distinct sites in primary silicate structures, and were considered to arise from Fe^{3+} substituting in the two distinct cis-octahedral sites (Johnston and Cardile, 1985), rather than from one Fe^{3+} site having an extremely varied range of environments, as considered here for montmorillonite.

In an electron diffraction study Tsipursky and Drits (1984) showed that 75–100% of the trans-octahedral sites are occupied in Wyoming and other montmorillonites in which the charge is localized in the octahedral layer. Therefore, the Fe^{3+} in the samples examined in the present study was apparently largely in the trans-

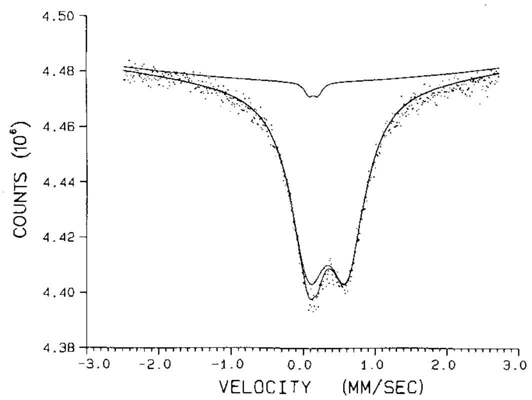

Figure 2. Experimental and computer-fitted ^{57}Fe Mössbauer spectrum for montmorillonite from Yavapai County, Arizona.

site, and the assignment of the most intense inner doublet to Fe^{3+} in the cis-octahedral site is incorrect. Instead, essentially only one octahedral resonance apparently was detected, which arose from the presence of Fe^{3+} mainly in the trans-octahedral site. This resonance was broadened because of the variable local geometry and complement of neighboring ions about this site, as discussed above. It is, of course, possible that some Fe^{3+} may have been present in the cis-octahedral sites (Drits *et al.*, 1984), but the extent was probably small.

A much less intense tetrahedral doublet was also computer-fitted to the Wyoming spectrum (Figure 1, Table 2). The linewidths of these peaks were slightly smaller than those of the experimental natural linewidths (about 0.21 mm/s) (Table 2). This artificially narrow linewidth was probably an artifact of trying to computer-fit a very minor component, using a Lorentzian lineshape model, to an experimental resonance which was broadened considerably as a result of the rather varied or disordered nature of the structure. A similar observation was noted for tetrahedral Fe^{3+} in nontronite from Garfield, Washington, if the experimental spectrum was not very well resolved (Johnston and Cardile, 1985). Also, such a tetrahedral Fe^{3+} component could not be distinguished in an untreated nontronite from Bingham Canyon, Utah, in which the low-velocity peaks of the two interlayer Fe^{2+} resonances overlapped closely with the two octahedral Fe^{3+} resonances. When the interlayer Fe^{2+} was removed by Ca-saturation, the model was simplified and this tetrahedral resonance was identified (Cardile and Johnston, 1985). From the asymmetry of the peak areas in the montmorillonite spectrum mentioned above, it appears that tetrahedral Fe^{3+} was definitely present in the structure. This result is interesting because in the past Fe^{3+} has not been considered to substitute in the tetrahedral sites of montmorillonite (see, e.g., Brindley and Brown, 1980). The tetrahedral sites are usually fully occupied by Si^{4+} or, in some montmorillonites by Si^{4+} and minor amounts of Al^{3+}. Although the isomer shift value for this tetrahedral Fe^{3+} doublet in montmorillonite was similar to that for nontronite, the quadrupole interaction value ($\Delta \approx 0.1$ mm/s; Table 2) was much smaller than that for nontronite (0.45 mm/s; Johnston and Cardile, 1985), suggesting that the neighboring environment around the Fe^{3+} in the tetrahedral layer was more symmetric in montmorillonite.

Recent work by Johnston and Cardile (1985) and Cardile and Johnston (1985) showed that Fe^{3+} can substitute in considerable amounts in the tetrahedral sites in nontronite. This substitution produces a large charge imbalance in the tetrahedral layer which, according to Tsipursky and Drits (1984), directs the further substitution of Fe^{3+} into the cis-octahedral sites leaving the trans-octahedral sites vacant. This substitution has been confirmed by Mössbauer spectroscopic measurements on a suite of nontronites (Johnston and Cardile, 1985; Cardile and Johnston, 1985). Conversely, in montmorillonite the small extent of substitution by Fe^{3+} in the tetrahedral sites, as compared with the octahedral sites, produces a charge imbalance in the octahedral layer which directs cation substitution within the octahedral layer to the trans-sites (Tsipursky and Drits, 1984).

The Mössbauer spectrum for the Yavapai montmorillonite could only be computer-fitted with a single prominent octahedral Fe^{3+} doublet comprising 98% of the overall resonance area and a very minor tetrahedral Fe^{3+} doublet (similar to that of Wyoming montmorillonite) comprising only 2% of the area (Figure 2, Table 2). The δ, Δ, and linewidth values for this octahedral doublet corresponded to those for the more prominent inner octahedral doublet of Wyoming montmorillonite. The asymmetry in the peak intensities definitely suggests the presence of tetrahedral iron, but here also because of the broadened nature of this spectrum, the linewidths of the tetrahedral doublet peaks were slightly below experimental natural linewidth (Table 2). Attempts to resolve the octahedral doublet further into two overlapping Fe^{3+} doublets using the additional width constraints, as discussed above for Wyoming montmorillonite, were unsuccessful. The spectrum for Yavapai montmorillonite did not show the same marked broadening at the base of the resonance, and, therefore, the sample was probably slightly more ordered structurally than the Wyoming sample. Here also, the iron in the octahedral layer was probably present as Fe^{3+} in the trans-octahedral sites.

The spectrum of the Husband Mine montmorillonite, shown in Figure 3, was computer-fitted with one octahedral doublet and a minor tetrahedral doublet giving a slightly high χ^2 value of 591 (Figure 3a, Table 2). Similar attempts to resolve this octahedral doublet further into two component doublets were only successful if all the octahedral doublet peak widths were constrained to be equal (Figure 3b). It is interesting to note that in the one-octahedral doublet model the linewidth of the tetrahedral Fe^{3+} resonance is acceptably larger than the experimental natural linewidth value (Table 2), whereas for the two-octahedral doublet model, it is not. This observation further emphasizes the effect that the fitting of an outer octahedral doublet to compensate for the spectral broadening had on the linewidth of the tetrahedral doublet. The respective areas for the two constrained octahedral doublets were consistent with those for the similarly constrained fit for Wyoming montmorillonite. The Δ value for the outer octahedral doublet for the Husband Mine sample, however, was smaller than the respective value for the Wyoming sample (Table 2); hence, the Husband Mine montmorillonite appears to be more ordered structurally.

If sufficient iron is present in the structure and the spectrum is recorded to a suitably high background count, the χ^2 value also reflects the extent of disorder within the structure, as observed in some nontronites (Johnston and Cardile, 1985). In montmorillonite, however, the iron content was too low for this effect to be used. Instead, the significantly high linewidths illustrate such structural disorder. Thus, the Fe^{3+} in the Husband Mine montmorillonite was apparently present mainly in the trans-octahedral site with a minor amount of Fe^{3+} in the tetrahedral sites and the structure was more ordered than that of Wyoming montmorillonite.

The spectrum of the Husband Mine sample heated to 453 K is shown in Figure 3c. According to separate thermogravimetric analysis data the interlayer water was removed at this temperature, but no dehydration of the structure occurred. X-ray powder diffraction showed that at 453 K the basal spacing collapsed to 10 Å, and that when the montmorillonite sample was allowed to cool to 298 K and rehydrated, the basal spacing expanded to its initial value of 15.3 Å. This dehydration-rehydration reaction was repeated several times, showing the process to be completely reversible. The spectrum of the heated sample was computed-fitted with two octahedral and a tetrahedral doublet requiring only the widths and dips of the component peaks of each doublet to be constrained equal (Figure 3c, Table 2). An acceptable $\chi^2 = 501$ was obtained for this fit. The Δ values for the inner octahedral doublet and, more particularly, the outer octahedral doublet were smaller than those respective values for any of the other unheated montmorillonites. Also, the relative area of the outer doublet increased considerably. Inasmuch as the quadrupole splitting of the tetrahedral doublet increased (Table 2), the electric field gradient exerted on the tetrahedral Fe^{3+} also increased because of the closer proximity of the interlayer cations which then resided in the pseudo-hexagonal cavities of the tetrahedral sheet. The neighboring tetrahedral sheet of the next layer was also closer. This configuration in turn exerted a greater influence on the octahedrally coordinated Fe^{3+} and enabled the spectrum to be resolved into two octahedral Fe^{3+} doublets. The narrower linewidths of these doublets suggests that as a result of the heating, the neighboring environments of the octahedral Fe^{3+} ions were more regular. It is unlikely that any amount of the Fe^{3+} ions would have migrated from the trans-octahedral sites into the cis-sites, but here also a range of different trans-sites may have been

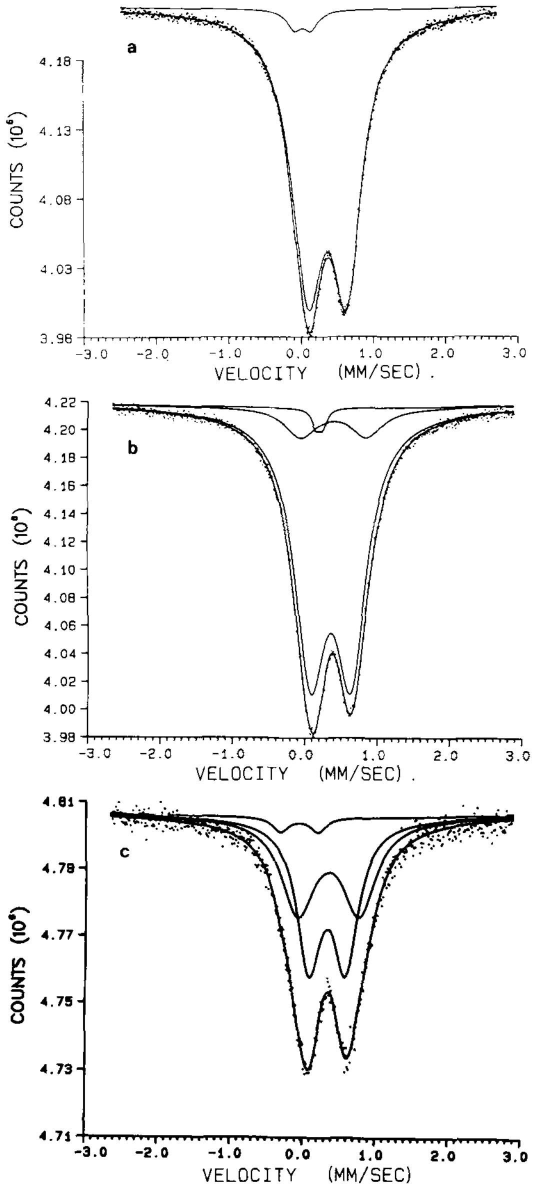

Figure 3. Experimental and computer-fitted ^{57}Fe Mössbauer spectra for montmorillonite from Husband Mine, Polkville, Mississippi: (a) one octahedral doublet and one tetrahedral doublet; (b) two octahedral doublets with the peak widths being constrained equal and a tetrahedral doublet; (c) spectrum recorded with the sample at 453 K.

present which were simply represented by a two-doublet fit. The increase in the intensity of the outer doublet appears to be related to the closer proximity of the interlayer cations to the octahedral Fe^{3+} ions. A similar effect has been observed in K-saturated nontronite wherein the basal spacing decreases from 15.4 Å for Ca-saturated nontronite to 12.22 Å for K-saturated nontronite and the area of the outer octahedral doublet increases accordingly (Johnston and Cardile, 1985). Hence, the interlayer and neighboring cations evidently influenced the Mössbauer resonance of iron in the octahedral sites in such smectites.

The iron content of the montmorillonites studied here varied from 2.23 to 5.44% Fe (Table 1). The computer-fitted Mössbauer data showed no discernible trends between the iron content and the Mössbauer spectrum; thus, the Fe^{3+} was essentially randomly distributed among the trans-octahedral sites, with a small proportion in the tetrahedral sites. The differences between the Mössbauer spectra for these samples, as discussed above, could have arisen from the possible clustering of Fe^{3+} within adjacent trans-octahedral sites as domains (Dickson and Cardile, 1985) or simply from the variability of such natural materials.

CONCLUSIONS

The Mössbauer spectrum of montmorillonite was found to be generally a considerably broadened Fe^{3+} resonance. This spectrum was computer-fitted with a similarly broadened Fe^{3+} doublet which, if certain constraints were used, was further resolved into overlapping inner and outer Fe^{3+} doublets, also with very broad linewidths. In accordance with electron diffraction evidence, the assignment by earlier workers of the inner doublet to Fe^{3+} in the octahedral site with a cis-arrangement of OH ions and the outer doublet to the trans-octahedral site appears to be incorrect. Instead, the Fe^{3+} appears to be located essentially in the trans-octahedral sites. Because of the relatively low iron content of montmorillonite, a considerable variation in the nearest and more distant types and geometrical arrangements of neighboring cations exists. This arrangement produces a significant line broadening in the experimental spectrum and the resulting two doublet computer-fits probably represent the mean extremes of a continuum of slightly different Fe^{3+} resonances arising from the variable nature of the environment surrounding these sites.

In addition, a small resonance indicating the presence of Fe^{3+} in the tetrahedral sites was noted. As with nontronite, the interlayer cations appear to influence the Mössbauer resonance of Fe^{3+} in the tetrahedral and octahedral sites.

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